



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B65D 81/34, 65/40, B32B 27/08, A22C 13/00</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/36798</b> <b>(43) International Publication Date:</b> 9 October 1997 (09.10.97)
<b>(21) International Application Number:</b> PCT/US97/05418 <b>(22) International Filing Date:</b> 1 April 1997 (01.04.97) <b>(30) Priority Data:</b> 617,720 1 April 1996 (01.04.96) US <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 08/617,720 (CIP) Filed on 1 April 1996 (01.04.96) <b>(71) Applicant (for all designated States except US):</b> W.R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036-7794 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BECKWITH, Scott, W. [US/US]; 847 Dorchester Road, Belton, SC 29627 (US). BEEKMAN, Dirk, D. [US/US]; 436 Riverside Chase Circle, Greer, SC 29651 (US). MIRLE, Srinivas, K. [US/US]; 4870-3 Dorsey Hall, Ellicott City, MD 21042 (US). RAMESH, Ram, K. [US/US]; 6 Rosebank Way, Greenville, SC 29615 (US).		<b>(74) Agents:</b> BURLESON, David, G. et al.; 100 Rogers Bridge Road, P.O. Box 464, Duncan, SC 29334 (US). <b>(81) Designated States:</b> CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> MODIFIER TRANSFER FILM AND METHOD OF COOKING A FOOD PRODUCT			
<b>(57) Abstract</b> <p>A film article suitable for cook-in packaging and a method of cooking a food product are described. The film article contains a food-contact layer which includes a copolymer which retains a food product modifier. The copolymer includes substantially water-insoluble segments and substantially hygroscopic segments. The copolymer is capable of transferring at least a portion of the modifier to a food product in contact with the food-contact layer. The film article is particularly well-suited for use as a cook-in film. In this regard, it is capable of sorbing and then transferring a modifier to a packaged food product in sufficient quantity that a separate, post-cooking application of modifier to the food product is unnecessary. Thus, only one package is necessary to cook, ship, and store the food product until it is to be consumed or further processed for retail display. Contamination risks associated with handling and repackaging a cooked food product can be altogether avoided.</p>			

## MODIFIER TRANSFER FILM AND METHOD OF COOKING A FOOD PRODUCT

### BACKGROUND INFORMATION

#### 5 1 Field of the Invention

This invention generally relates to packaging films and to processes employing such films. More specifically, this invention relates to films that can retain and then, during a cook-in process, transfer a modifier to a food product as well as to methods of cooking and transferring a modifier to a food product in  
10 such films.

#### 2 Background of the Invention

Food products often are processed in thermoplastic film packages by subjecting the packaged products to elevated temperatures. For example, such packaged products can be immersed in hot water or placed in a steam-heated  
15 environment. Such thermal processing often is referred to as "cook-in", and films used in such processes are known as cook-in films. The processed and packaged food product can be refrigerated, shipped, and stored until the processed food is to be consumed or, for example, sliced and repackaged into smaller portions for customer display (Many sliced luncheon meats are processed in this fashion.)  
20 Alternatively, the processed food can be removed immediately from the cook-in package and consumed or further processed for customer display (e.g., sliced and repackaged).

Cook-in films must be capable of withstanding exposure to rather severe temperature conditions for extended periods of time while not compromising their  
25 ability to contain the food product. Cook-in processes typically involve a long cook cycle. Submersion in hot water for up to about 4 hours at about 55° to 65°C is common, and submersion in water or steam at 70° to 100°C for up to 12 hours is possible.

Following the cook-in process, the film preferably conforms, if not  
30 completely then at least substantially, to the shape of the contained food product. Often, such conformation is achieved by allowing the film to heat shrink under

film, withstanding the rather extreme conditions involved in cook-in processes, and providing a sufficient level of adhesion with the packaged food product

Sufficient adhesion can be a particularly difficult requirement to meet. Specifically, the film must be able to prevent cook-out and also be removable from the food product once it is cooked. Some presently available cook-in films can prevent cook-out. However, such films tend to adhere to the surface of the food product with such tenacity that portions, or even an entire surface layer, of the food product are torn away when the film is peeled from the food product. As a result, product yield is reduced, and the resulting food product has an unsightly appearance (e.g., a pitted surface).

Because conventional cook-in films have not heretofore successfully transferred modifier to a food product during cook-in, any desired modifier generally must be applied to the food product after the cook-in process. This necessitates stripping the cook-in film from, applying the modifier to the surface of, and then repackaging the cooked food product which adds time, expense, and complexity to the cooking/packaging process. This procedure also increases the likelihood that the food product, which is sterilized by the cooking process, will become contaminated. Eliminating the necessity of removing the food product from its cook-in package, handled, and potentially exposed to microbial contact prior to its consumption or processing for retail display is highly desirable.

Accordingly, a need exists for a cook-in packaging film that can facilitate the transfer of a modifier to a food product during the cook-in process, minimize or prevent cook-out, and yet still peel away from the food product without tearing portions from the surface thereof.

## SUMMARY OF THE INVENTION

Briefly, the present invention provides a film article having a food-contact layer that includes a copolymer with a modifier retained therein. The copolymer includes segments that are substantially insoluble in water and other segments that are substantially hygroscopic. The copolymer retains the modifier in such a

To assist in understanding the more detailed description of the invention that follows, certain definitions are provided immediately below. These definitions apply hereinthroughout unless a contrary intention is explicitly indicated

5 "polymer" means the polymerization product of one or more monomers and is inclusive of homopolymers, copolymers, terpolymers, tetrapolymers, etc., and blends and modifications of any of the foregoing;

"mer unit" means that portion of a polymer derived from a single reactant molecule (e.g., a mer unit from ethylene has the general formula  $\text{—CH}_2\text{CH}_2\text{—}$ );

10 "homopolymer" means a polymer consisting essentially of a single type of repeating mer unit;

"copolymer" means a polymer that includes mer units derived from at least two reactants (normally monomers) and is inclusive of random, block, segmented, graft, etc., copolymers;

15 "polyvinyl alcohol", abbreviated herein as "PVOH", means the material formed by partial or complete hydrolysis of poly(vinyl acetate);

"hydroxy propyl cellulose", abbreviated herein as "HPC", means a thermoplastic, non-ionic cellulose ether formed by the reaction of propylene oxide with alkali cellulose slurried with an aliphatic hydrocarbon and alcohol or propylene oxide;

20 "polyolefin" means a polymer in which some of the resulting mer units are derived from an olefinic monomer, which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted (e.g., olefin homo-polymers, copolymers of two or more olefins, copolymers of an olefin and a non-olefinic comonomer such as a vinyl monomer, and the like);

25 "(meth)acrylic acid" means acrylic acid and/or methacrylic acid;

"(meth)acrylate" means acrylate and/or methacrylate;

"(meth)acrylamide" means acrylamide and methacrylamide;

"anhydride-modified polymer" means one or more of the following:

30 (1) a polymer obtained by copolymerizing an anhydride-containing monomer with a comonomer, (2) an anhydride-grafted copolymer, and (3) a mixture of a polymer and an anhydride-containing compound;

includes modified polyolefin and/or polyurethane, more preferably at least one of modified ethylene/ $\alpha$ -olefin copolymer, modified ethylene/unsaturated ester copolymer, and modified ethylene/unsaturated acid copolymer. Anhydride-modified ethylene/ $\alpha$ -olefin copolymer and anhydride-modified

5 enthylene/unsaturated ester copolymer are particularly preferred. Specific examples include anhydride-grafted linear low density polyethylene (LLDPE) or anhydride-grafted ethylene/vinyl acetate copolymer.

With respect especially to films to be used for cook-in processes, one exterior layer acts as a food-contact layer while the other acts as an outer layer.

10 The former serves as the inner layer of a package formed from the film and is in direct contact with the packaged food product. The latter provides abuse resistance by serving as the outer layer of the package, i.e., that layer which is most distant from the food-contact layer.

To form a multilayer film, the individual layers are laminated, i.e., bonded

15 together. Lamination can be accomplished through the use of adhesives, the application of heat and/or pressure, corona treatment, and even spread or extrusion coating. Lamination also can be accomplished by coextrusion, which involves extruding two or more materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a laminar structure

20 before cooling. Coextrusion can be employed in film blowing, free film extrusion, and extrusion coating processes

Some films, including many which are used in cook-in processes, are oriented prior to use. Orientation involves stretching a film at an elevated temperature (the orientation temperature) followed by setting the film in the stretched configuration

25 (e.g., by cooling). When an unrestrained, unannealed, oriented polymeric film subsequently is heated to its orientation temperature, heat shrinkage occurs and the film returns almost to its original, i.e., pre-oriented, dimensions.

An oriented film has an orientation which is the multiplication product of the extent to which the film has been expanded in several directions, usually two directions

30 perpendicular to one another. Expansion in the longitudinal direction, sometimes referred to as the machine direction, occurs in the direction the film is formed during

the copolymer and thereby maintain the integrity of the food-contact layer during cook-in

Thus, a copolymer including both water-insoluble and hygroscopic segments advantageously (1) allows for sorption and subsequent transfer (to a food product during cook-in) of a modifier, and (2) remains intact (or at least substantially intact) so that the food-contact layer can be separated from the food product at any desired time after cooking.

The relative amounts of water-insoluble and hygroscopic segments in the copolymer can be selected to provide any desired balance of water insolubility and hygroscopicity. Generally, the water-insoluble segments can be present in the copolymer at a weight percentage ranging from about 1 to about 99 while the hygroscopic portions can be present at a weight percentage ranging from about 99 to about 1; more preferably, the water-insoluble segments can be present at a weight percentage ranging from about 20 to about 95 while the hygroscopic segments can be present at a weight percentage ranging from about 80 to about 5; most preferably, the water-insoluble portions can be present at a weight percentage ranging from about 40 to about 90 while the hygroscopic portions can be present at a weight percentage ranging from about 60 to about 10.

Preferably, the water-insoluble segments of the copolymer have a solubility in an aqueous medium of less than 10%, more preferably less than 5%, more preferably still less than 1%, even more preferably less than 0.1%, yet more preferably less than 0.05%, more preferably still less than 0.01%, even more preferably less than 0.005%, and most preferably less than 0.001%. (All of the foregoing percentages are weight percentages.) The water-insoluble segments preferably are derived from one or more of amides, olefins, esters, alkyl (meth)acrylates, vinyls, dienes, alkynes, lactides, sulfides, sulfones, urethanes, siloxanes, and silanes. Of the foregoing, amides, olefins, and esters are particularly preferred, with amides such as nylon 6, nylon 6/6, nylon 12, nylon 6/12, and the like being most preferred.

The hygroscopic segments of the copolymer preferably have a water sorption capacity of greater than 5%, more preferably greater than 10%, more

any desired amount depending upon the particular application for which the film article is to be used. The copolymer can include between about 1 to 99 weight percent mer units derived from an ether and between about 99 to 1 weight percent mer units derived from an amide. Preferably, however, the copolymer includes between  
5 about 20 to 80 weight percent mer units derived from an ether and between about 80 to 20 weight percent mer units derived from an amide.

A particularly preferred type of ether/amide copolymer is a block copolymer, i.e., poly(ether block amide) (PEBA). This type of block copolymer can be produced from a molten state polycondensation of a dicarboxylic  
10 polyamide and a polyether diol. Preferred PEBA's include PEBAX™ MX 1074 and 6031 (Elf-Atochem North America, Inc., Philadelphia, PA), both of which contain blocks of nylon 12 and poly(ethylene glycol).

In accordance with another embodiment of the invention, the food-contact layer can include HPC or a blend of HPC and another polymer. Commercially  
15 available HPCs include Klucel™ (Aqualon Division of Hercules, Inc., Wilmington, Del.) and Nisso™ resins (Nippon Soda Co. Ltd., Tokyo, Japan).

Chemical or radiative crosslinking of the HPC to an extent sufficient to render the food-contact layer substantially water insoluble is preferred. In this manner, the HPC food-contact layer remains intact and does not dissolve into the  
20 food product. Preferred chemical crosslinking agents include, e.g., aldehydes, diisocyanates, glyoxal, boric acid, and sodium borate. Radiative crosslinking means are well known to those of ordinary skill in the art.

In general, the food-contact layer can have a thickness ranging from about 0.25 to 250  $\mu\text{m}$  (0.01 to 10 mils), preferably from 1.3 to 25  $\mu\text{m}$  (0.05 to 1 mil), more  
25 preferably from 2.5 to 13  $\mu\text{m}$  (0.1 to 0.5 mils), and most preferably from about 5 to 7.5  $\mu\text{m}$  (about 0.2 to 0.3 mils).

To withstand cook-in time and temperature conditions, the polymer(s) from which the food-contact layer is formed preferably has/have a melting point ranging from about 70° to 250°C, more preferably from about 85° to 230°C, even more  
30 preferably from about 100° to 200°C, and most preferably from about 120° to 180°C.

To assist in reducing or eliminating cook-out, a food-contact layer having a surface energy of greater than 34 dynes/cm, preferably greater than 38 dynes/cm, more preferably greater than 42 dynes/cm, even more preferably greater than 46 dynes/cm, and most preferably greater than 50 dynes/cm is preferred. At such surface energies, the food-contact layer is believed to provide sufficient adhesion with the food product to prevent or substantially minimize cook-out.

*high corona treatment*

If the film adheres so strongly to the cooked food product such that it cannot be peeled therefrom without tearing away portions of the same, the copolymer of the food-contact layer can be blended with one or more polymers that lower its adhesion. In this regard, less polar polymers such as polyolefins having a surface energy of about 36 dynes/cm or less can provide beneficial results. On the other hand, if adhesion between the film article and food product is too low, the surface energy of the food-contact layer can be increased. This can be accomplished by, for example, subjecting the surface of the food-contact layer to sufficient energetic radiation (i.e., of sufficiently high intensity or for a sufficiently long period of time) to achieve a desired increase in surface energy. Examples of radiative techniques include plasma and corona treatments. Alternatively, the surface energy of the food-contact layer can be increased by including one or more polar additives such as polyesters, polyamides, polylactic acid, and polar polyolefins such as ethylene/unsaturated acid copolymers, modified polyolefins, and blends thereof.

When formed into a food-contact layer, PEBA advantageously has been found to provide sufficient adhesion with a packaged food product during cook-in to substantially prevent cook-out without the need for corona treatment. At the same time, adhesion between PEBA and the food product is sufficiently low that the film article can be peeled from the food product after cook-in without substantial tearing of particles from the food product.

As mentioned previously, modifiers are substances that can change the odor, color, taste, texture, etc., of a packaged product. Normally, the modifier effects a change in the surface of the product to which it is applied when sorbed by that surface. This sorption can occur either without, but preferably with (in the



fabricated into a bag, the modifier can be added by simply filling the bag or, as disclosed in U.S. Pat. No. 5,484,001, partially filling the bag and then squeezing the modifier between a moveable external roller and backing plate so that it is dispersed along and absorbed into a desired portion of the inside (i.e., food-

5 contact layer) of the bag. Other means for sorbing the modifier into the food-contact layer include soaking the food-contact layer in a modifier or modifier mixture and then laminating it to the rest of the film structure; coating a modifier solution onto the food-contact layer by means of, for example, a flexographic printing press, a doctor blade, gravure coating, reverse roll coating, etc.; or

10 spraying a modifier solution into the inside of a tube or bag formed from the film article.

Surprisingly, the food-contact layer of the film article of the present invention has been found to be capable of sorbing, retaining, and then transferring a relatively large amount of modifier as a percentage of the total weight of the

15 food-contact layer. For example, a multilayer film having a PEBA food-contact layer that constitutes approximately 10% of the film's total weight and thickness, can sorb and retain between about 50 and 250 weight percent of a liquid smoke modifier, based on the total weight of the multilayer film. If expressed as a percentage of the weight of the PEBA layer alone, the sorption ranges from about

20 500 to 2500 weight percent. The amount of modifier retained by the food-contact layer often can vary with the viscosity of the modifier. Generally, lower viscosity modifiers are sorbed and retained to a greater degree than higher viscosity modifiers.

The values provided in the foregoing paragraph are based on the amount

25 of modifier retained by the food-contact layer shortly after soaking the film article in a liquid smoke solution, i.e., with little or no drying of the film article. However, where a film article is allowed to dry (e.g., at room temperature for a period of 12 to 18 hours), the amount of liquid smoke modifier retained by the food-contact layer is somewhat lower. For a multilayer film having a PEBA food-

30 contact layer, the amount of modifier retained after drying ranges from about 20

modifier retained in the food-contact layer of a film article of the present invention is believed to be transferred to a food product cooked in the film article.

The film article of the present invention can have a single layer or include a number of layers. Preferably, the film article is a multilayer film having an outer  
5 layer comprising at least one of polyolefin, polystyrene, polyamide, polyester, poly(ethylene/vinyl alcohol), polyvinylidene chloride, polyether, polyurethane, and polycarbonate. The outer layer preferably provides abuse resistance to the film article when it is formed into a cook-in package. Polyolefins and/or polyamides often prove to be particularly useful in this regard.

10 Suitable polyolefins include polyethylene homopolymer or copolymer, polypropylene homopolymer or copolymer, and polybutene homopolymer or copolymer. Preferred examples include ethylene/ $\alpha$ -olefin copolymer, propylene/ $\alpha$ -olefin copolymer, butene/ $\alpha$ -olefin copolymer, ethylene/  
unsaturated ester copolymer, and ethylene/unsaturated acid copolymer. Specific  
15 examples of preferred polyolefins include one or more of LLDPE, ethylene/vinyl acetate copolymer (EVA), propylene/ethylene copolymer, and propylene/butene copolymer. An ethylene/ $\alpha$ -olefin copolymer includes mer units derived from ethylene and from one or more  $C_3$  to  $C_{20}$   $\alpha$ -olefins such as 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, and the like. The resulting polymer  
20 molecules include long chains with relatively few side chain branches and the side branching that is present is short compared to non-linear polyethylenes (e.g., low density polyethylene homopolymer). Ethylene/ $\alpha$ -olefin copolymers generally have a density in the range of from about 0.86 g/cc to about 0.94 g/cc. LLDPE  
generally is understood to include that group of ethylene/ $\alpha$ -olefin copolymers  
25 which fall into the density range of about 0.915 to about 0.94 g/cc. Sometimes, linear polyethylene having densities of from about 0.926 to about 0.94 are referred to as linear medium density polyethylene (LMDPE). Lower density ethylene/ $\alpha$ -olefin copolymers can be referred to as very low density polyethylene (VLDPE, typically used to refer to ethylene/butene copolymers available from Union  
30 Carbide with a density ranging from about 0.88 to about 0.91 g/cc ) and ultra-low

If the outer layer comprises polyamide, adding polymers that are compatible with the polyamide or polyamide blend so as to modify the properties of the polyamide can be beneficial for some applications. Suitable polymers include polyolefins, such as those incorporating acids, esters, anhydrides or salts of carboxylic acids; and polar, non-polyolefinic materials such as polyesters, EVA, etc.

If desired, additional layers can be included as interior layers. Preferred materials from which such interior layers can be formed include polyolefin, particularly EVA, ethylene/alkyl acrylate copolymer (e.g., ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate, etc.), LDPE, and ethylene/ $\alpha$ -olefin copolymer (e.g., LLDPE or VLDPE); polyamide; polyurethane; and blends of any of the foregoing. In addition, any of the materials described above as suitable for use in the outer layer also can be used to form one or more interior layers.

If desired, the film article can contain an interior layer that acts as a barrier. (Barrier layers inhibit the transmission of one or more gases, e.g.,  $O_2$ .) Such a layer can be advantageous for extending the shelf-life of an oxygen-sensitive product, such as beef, poultry, pork, or fish, when packaged in the film article of the present invention. Such an oxygen barrier layer preferably is formed from at least one material selected from the group consisting of ethylene/vinyl alcohol copolymer, vinylidene chloride copolymer, polyamide, PVOH, polyhydroxyaminoether, polyalkylene carbonate, or a blend of any of the foregoing. If desired, oxygen barrier functionality also or alternatively can be provided by appropriate material selection for the outer layer or other interior layers.

Each of the foregoing materials from which the film article can be constructed are commercially available from a number of suppliers. Specific examples are listed in the Examples below

If heat shrinkable, the film article preferably has a free shrink at 85°C (185°F), determined according to ASTM D 2732, of from about 5 to 70%, more preferably from about 10 to 50%, and most preferably from about 15 to 35% in at

FC: food-contact layer, as described above;

PA: polyamide-containing layer, preferably having a thickness of from 2.5 to 130  $\mu\text{m}$  (0.1 to 5 mils), more preferably from 5 to 75  $\mu\text{m}$  (0.2 to 3 mils), most preferably from 13 to 25  $\mu\text{m}$  (0.5 to 1 mils);

5 PO: polyolefin-containing layer, preferably having a thickness of from 2.5 to 130  $\mu\text{m}$  (0.1 to 5 mils), more preferably from 5 to 75  $\mu\text{m}$  (0.2 to 3 mils), most preferably from 13 to 25  $\mu\text{m}$  (0.5 to 1 mils);

B: oxygen barrier layer, preferably having a thickness of from 0.25 to 130  $\mu\text{m}$  (0.01 to 5 mils), more preferably from 1.3 to 13  $\mu\text{m}$  (0.05 to 0.5 mils), most preferably from 2.5 to 7.5  $\mu\text{m}$  (0.1 to 0.3 mils); and

10 TIE: tie layer having a preferred thickness of 0.25 to 25  $\mu\text{m}$  (0.01 to 1 mils), more preferably 1.3 to 13  $\mu\text{m}$  (0.05 to 0.5 mils), most preferably 2.5 to 7.5  $\mu\text{m}$  (0.1 to 0.3 mils).

In the following film structures, the individual layers are shown in the order in which they would appear in the film:

	FC (monolayer)
	FC / PA
	FC / PO
	FC / TIE / PO
20	FC / B / PA
	FC / TIE / PA
	FC / PO / PA
	FC / B / PO
	FC / TIE / B / PO
25	FC / TIE / B / TIE / PO
	FC / PA / B / PA
	FC / TIE / PO / TIE / PA
	FC / TIE / B / TIE / PA
	FC / TIE / PA / TIE / PA
30	FC / TIE / B / PA / TIE / PA

The food product is placed inside of the bag or casing and the opening is sealed closed, e.g., by heat-sealing or clipping, so that the resultant enclosure is substantially liquid-tight. The enclosed food product is then heated for a time and at a temperature sufficient to at least partially, but preferably fully, cook the food product. During this process, at least some of the modifier retained within the food-contact layer is transferred to the food product. Any suitable means of heating can be employed, including immersing the enclosed food product in a bath of heated water or steam, or placing the enclosed food product in a hot air or steam cabinet. In one preferred embodiment, the film article is heat shrinkable so that the food-contact layer will be in close contact with the food product, thereby facilitating transfer of the modifier. If the film is not heat shrinkable, the inside of the bag or casing can be evacuated and collapsed against the food product prior to sealing the bag or casing closed.

After the desired degree of cooking has been achieved, the processed and packaged food product is removed from the heating means and allowed to cool. The film article can be stripped from the food product at any desired time after the cooking process has been completed. That is, the film article immediately can be stripped and the food product then can be either consumed or further processed, e.g., sliced and repackaged into smaller portions for customer display by a retailer. Alternatively, the processed and packaged food product can be refrigerated, shipped to a retailer, and stored until the processed food is to be consumed or further processed as described above.

Food products which can be packaged and cooked in accordance with the present invention can be any of those foods which are amenable to cook-in packaging, including whole muscle or chopped red meat, poultry, pork, or fish. Also included are foods which are not intended to be cooked-in but simply stored within the package, during which time a modifier is to be transferred to the packaged food product. Such foods include cheese, vegetables, fruits, and already cooked meat, poultry, pork, or fish. In general, however, the invention is most advantageous when used as a cook-in package for, e.g., poultry, ham, beef, lamb,

the tube having a lay flat width of about 16.5 cm (6.5 in.), with the multilayer film having a total thickness of 56  $\mu$ m (2.2 mils).

The resulting film had about 20% free shrink in the longitudinal direction and about 30% free shrink in the transverse direction when immersed in hot water  
5 at 85°C (185°F) using ASTM method D 2732-83.

#### Example 2

Multilayer films made according to the teaching of Example 1 and monolayer PVOH films were subjected to cook-in testing by soaking  
10 15 cm  $\times$  15 cm (6 in.  $\times$  6 in.) film samples in a Charsol Select™ 24 liquid smoke solution having a pH of 2.4 (Red Arrow Products Co., Inc., Manitowoc, WI) for a predetermined period of time ranging from 1 to 10 minutes to allow the PEBA or PVOH food-contact layer to sorb some of the liquid smoke. Some of the samples were simply shaken dry and then weighed to determine the amount of liquid smoke  
15 absorbed by the food-contact layer. Others were allowed to dry for at least 12 hours before weighing. This was done to replicate actual use conditions where, in some instances, the food-contact layer is impregnated with modifier shortly before packaging a food product (and will therefore be wet with modifier solution during the transfer of the modifier to the food product) and in other instances the  
20 modifier-soaked food-contact layer is dried by the time a food product is packaged in the film article.

A chicken breast emulsion having 3% salt, 0.5% phosphate, and 35% water, the balance being defatted chicken breast meat (all percentages based on the total weight of chicken breast), was prepared. Sections of 10 cm (4 in.)  
25 diameter poly(vinyl chloride) pipe were stuffed with the chicken breast emulsion and capped on one end with a 15 cm  $\times$  15 cm sample of liquid smoke-impregnated film. The other end was capped with a control film having a food-contact layer comprising a 50:50 blend of nylon 12 and nylon 6/12. The control film did not contain modifier but was used as a basis for comparison of the meat-  
30 adhesion/cook-out prevention capabilities of the films of the present invention.

Table 1

	PEBA	PEBA	PVOH-1 <sup>a</sup>	PVOH-2 <sup>b</sup>
Soak time (min)	1	10	1	5
Initial film wt. (g)	9.35	9.65	1.65	1.72
Dry film wt. <sup>c</sup> (g)	12.19	12.39	4.28	5.55
Modifier sorbed <sup>d</sup> (wt. %)	30.4	28.4	159	222
Adhesion <sup>e</sup>	moderate	moderate	low	low
Transfer <sup>f</sup>	good	good	good	good

a) M1030 PVOH (Mono-Sol Division of Chris-Craft, Inc., Gary, Indiana)

b) M1040 PVOH (Mono-Sol Division of Chris-Craft, Inc.)

5 c) The weight of the film after being dried for at least twelve hours after being soaked in a liquid smoke solution.

d) The amount of modifier retained by the food-contact layer expressed as a percentage of the initial, pre-soaked weight of the film.

10 e) A qualitative measure of the degree to which the food-contact layer adhered to the surface of the cooked chicken product and prevented cook-out. "Very high" represents essentially no cook-out but substantial tearing of chicken upon removal of the film; "high" represents essentially no cook-out and only some tearing of chicken upon removal of the film; "moderate" represents little or no cook-out and no tearing of chicken upon removal of the film; "low" represents some cook-out and no tearing; and "none" indicates no adhesion with substantial cook-out. The comparative film having a blend of nylon 6 and nylon 6/12 for the food-contact layer exhibited "very high" to "high" adhesion under this rating system.

15 f) A qualitative measure of the degree to which the food-contact layer transferred liquid smoke to the chicken. "Good" indicates a high degree, "fair" indicates a moderate degree, and "poor" indicates a low degree of transfer.

20

Table 2 sets forth test results for films samples which had not been dried prior to commencement of the cook-in procedure.

The casings were stuffed with a meat emulsion consisting of about 30-45% boneless, skinless turkey breast, 50-65% water, 2% NaCl, 0.5% sodium tripolyphosphate, 2% carrageenan, and 1% tapioca starch (all percentages being weight percentages). These stuffed casings were clipped to form a substantially liquid-tight enclosure and placed in a high-humidity thermal processing unit to cook the meat emulsion. Cooking temperatures ranged from 60° to 82°C (140° to 180°F).

The meat emulsions were weighed before and after cooking to determine the amount purge loss (i.e., cook-out) resulting from the cook-in process. After cooking, the stuffed casings were chilled and then the casings were stripped from the cooked meat product. Observations were made regarding meat adhesion, modifier transfer, and color uniformity of the surface of the modified and cooked meat product.

The test results are summarized in Table 3, wherein each value is an average from three identically-tested samples.

Table 3

	LS-1 <sup>a</sup>	LS-2 <sup>b</sup>	LS-3 <sup>c</sup>
Initial casing wt. (g)	9.28	9.64	9.09
Final casing wt. <sup>d</sup> (g)	11.75	12.20	12.12
Modifier sorbed (wt %)	26.6	26.6	33.3
Initial meat wt. (kg)	1.12	1.13	1.06
Cooked meat wt. (kg)	1.10	1.13	1.05
Percent cook-out <sup>e</sup>	1.2	0.4	0.85
Adhesion	low/none	low/none	low
Transfer	good	good	fair
Uniformity <sup>f</sup>	mottled	uniform	uniform

a) LFBN Liquid Smoke having a pH of 6.1 (Red Arrow Products Co.)

20 b) N52 Liquid Smoke having a pH of 5.4 (Red Arrow Products Co.)

c) Select 55 Liquid Smoke having a pH of 5.5 (Red Arrow Products Co.)



That which is claimed is:

1. A film article comprising a food-contact layer, said food-contact layer comprising:
  - 5 a) a copolymer comprising substantially water-insoluble segments and substantially hygroscopic segments, and
  - b) a modifier retained by said copolymer,at least a portion of said modifier being capable of transferring from said copolymer to a food product in contact with said food-contact layer.
- 10 2. The film article of claim 1 wherein said substantially water-insoluble segments are derived from one or more of amides, olefins, esters, alkyl (meth)acrylates, vinyls, dienes, alkynes, lactides, sulfides, sulfones, urethanes, siloxanes, and silanes.
- 15 3. The film article of claim 2 wherein at least some of said substantially water-insoluble segments are derived from one or more of an amide, an olefin, and an ester.
- 20 4. The film article of claim 3 wherein at least some of said substantially water-insoluble segments are derived from an amide
- 5 The film article of claim 4 wherein said amide is one or more of nylon 6, nylon 12, nylon 6/6, and nylon 6/12.
- 25 6. The film article of claim 1 wherein said substantially hygroscopic segments are derived from one or more of ethers, celluloses, saccharides, anhydrides, caprolactones, imines, (meth)acrylic acid, (meth)acrylamides, cinnamides, succinimides, piperidines, vinyl acetates, vinylpyrrolidones, vinyloxazolidones, sulfonic
- 30 acids, phosphoric acids, phosphonic acids, silicic acids, vinylamines, vinyl sulfuric acids, maleic acid, benzoic acids, and phenols.
7. The film article of claim 8 wherein at least some of said substantially hygroscopic segments are derived from an ether.

as to at least partially cook said food product, whereby at least some of said modifier is transferred from said food-contact layer to said food product.

18 A method for making a multilayer film having a food-contact layer  
5 which contains therein a modifier, said method comprising the step of laminating on a film article a food-contact layer impregnated with a solution comprising a modifier.

19 A method for impregnating a food-contact layer with a modifier, said  
10 method comprising the step of coating a solution comprising a modifier onto said food-contact layer so that at least a portion of said modifier is retained by said food-contact layer

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 97/05418

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 855 183 A (OBERLE TIMOTHY T) 8 August 1989 see column 4, line 18 - line 46; examples -----	1

...ormation on patent family members

PCT/US 97/05418

Form PCT/ISA 210 (patent family annex) (July 1992)